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Detection of charge transfer processes in Cr-doped $SrTiO_3$ single crystals

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An insulator-to-metal transition is observed in Cr-doped $SrTiO_3$ single crystals upon extended exposure to a high electric field, namely, electroconditioning (EC). Electron paramagnetic resonance (EPR) and transport measurements under laser irradiation show anticorrelation between the Cr^{3+} EPR signal and the electrical current. This proves that the Cr^{3+} ions are responsible for the photocurrent that initiates the EC process. We observe the presence of Cr^{3+}/Cr^{4+} mixed valencies in the bulk in the conducting state. The EPR characterization of the spectra in the conducting state excludes the possibility of a Cr^{3+}-oxygen vacancy complex in the bulk as a result of the EC. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2959059]

Insulator-to-metal transitions with a resistive memory effect in selected perovskites are under intense investigation because of potential applications for information storage devices (Ref. 1, and references therein). The investigation of insulating Cr-doped $SrTiO_3$ (band gap=3.2 eV) as model system shows that during exposure to an electric field[1–3] its resistance is reduced by several orders of magnitude and a conductive state is reached. We define this process as electroconditioning (EC). In the conducting state, current pulses of opposite polarity switch the resistance reversibly between a high and a low level.[2,4,5] So far, it is not clear whether the fundamental switching mechanism is an interface effect, a bulk effect, or a combination of both. Understanding the mechanism of the EC process is crucial for the development of a model describing the behavior of such a system.

In our study we investigate the influence of the Cr dopant during the EC process. We discuss results obtained on crystals with a doping concentration of 0.1 and 0.2 mol %, grown by the floating-zone method, and annealed for 6 h at 1150 °C in $Ar/H_2(5\%)$. Capacitor-like structures of dimensions $2.5\times1\times0.2$ mm^3 were prepared by depositing Pt electrodes of 50–100 nm thickness on the (100) large faces of polished crystals via e-beam evaporation. The electrodes consist of 0.1×2 mm^2 stripes with a gap of 0.15 mm, interconnected by drops of silver paint to form a meandering structure. These structures are an approximation of a continuous metallic layer, but are transparent to microwave radiation. Electron paramagnetic resonance (EPR) spectra at 9.4 GHz were collected with a Bruker EMX™ spectrometer, and a 2,2-diphenyl-1-picrylhydrazyl sample was used both as standard for the intensity and as a reference resonance marker. A 633 nm (~1.9 eV) laser of 10 mW was used to illuminate the sample in combination with an optical shutter. Luminescence was detected by means of an avalanche photodiode collecting photons in the range of 400–1100 nm.

We started the EC process with crystals that were insulating despite of having been annealed in reducing atmosphere. It is known that in $SrTiO_3$ oxygen vacancies (V_O) introduced by a reduction process create a conducting state.[6] However, in our case, because of the presence of the Cr dopants, the insulating state is preserved via a charge compensation by transforming the initial Cr^{4+} to Cr^{3+} (Ref. 2). The Cr^{3+} ions act as a reservoir of electrons which can be promoted selectively to the conduction band (CB) by photoexcitation above ~1.86 eV.[7] This process can be directly observed in the time dependence of the photocurrent and the EPR signal of Cr^{3+} under laser irradiation. This is shown in Fig. 1 for a virgin crystal with 0.1 mol % of Cr at fixed bias voltage of 50 V. The photocurrent under laser illumination is accompanied by a decrease in the Cr^{3+} signal. After stopping the irradiation, the CB electrons recombine at the Cr centers, as evidenced by the recovery of the EPR signal. Simultaneously, the current drops rapidly to the initial value. This anticorrelation is a direct proof of selective transfer of electrons between the Cr ions and the CB. Further evidence of this recombination process is provided by the delayed luminescence (DL) which accompanies the EPR signal recovery (Fig. 1). This emission arises when a CB electron is trapped by Cr^{4+}, forming Cr^{3+} in an excited state ($^2E_{2g}$), which subsequently relaxes radiatively via the $^2E_{2g}\rightarrow{}^4A_{2g}$ transition (R line, see Fig. 2).[2,7,8] A part of the electrons are fast in recombining and the rest need a longer time to diffuse until

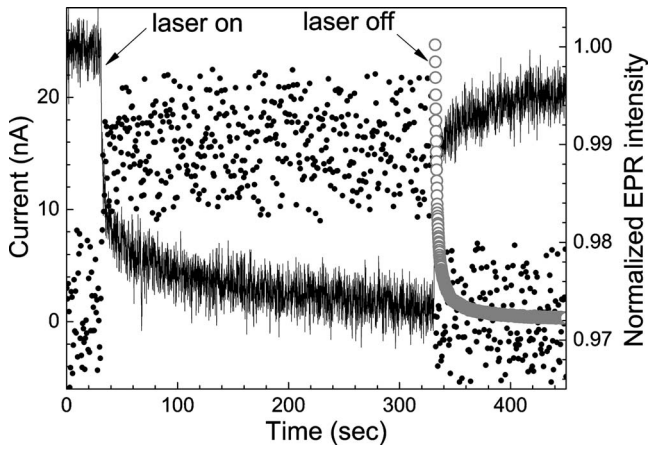

FIG. 1. Photocurrent (dots) and EPR intensity of Cr^{3+} (continuous line) in Cr-doped $SrTiO_3$ ([Cr]=0.1 mol %) as a function of time for a bias voltage of 50 V and laser irradiation (λ=633 nm). When the laser is turned off, the DL arising from the R line of Cr^{3+} is recorded (gray open circles). The EPR data are not corrected for a slow linear drift.

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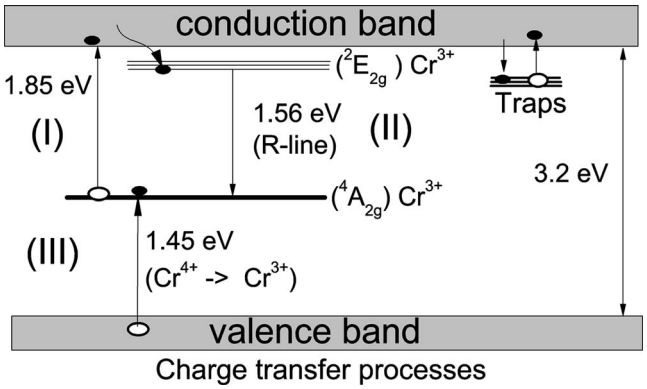

FIG. 2. Diagram of energy transitions and charge transfer processes involving the Cr^{3+} ions in $SrTiO_3$. Adapted from Basun *et al.* (Ref. 7).

they recombine at Cr sites. The recovery of the EPR signal exhibits two components: the fast one correlated with the current drop and the slow one also visible in the DL measurements. The EPR signal indicates that roughly half of the electrons recombine promptly, whereas the remainder recombines with a very long decay time. The slow recombination kinetics was proposed by Basun *et al.*[7] to originate from the capture of electrons at trap centers below the CB, which are not related to the Cr, and by their release, which can be activated thermally and/or by IR irradiation (<1 eV).[7] Figure 2 shows an additional charge transfer process (III) from the valence band (VB) to Cr^{4+}, resulting in the increase of the Cr^{3+} concentration and creation of holes in the VB. As in the virgin sample all Cr ions are in the 3+ state at the beginning of the irradiation, process III is negligible. However, the creation of Cr^{4+} via process I will be balanced via processes II and III as shown by the asymptotic approach to a steady state in the EPR signal (see Fig. 1). The rate of recombination of process II is controlled by the diffusion of electrons from the traps. The time to reach 90% of both EPR signal decay and recovery is comparable and on the order of 80 s. At high initial resistance (~ 30 GΩ), process I provides the carriers necessary to initiate the EC, which typically requires fields higher than 10^4 V/cm. For prolonged application of such a bias under continuous photoexcitation, the current will increase, and the voltage is adjusted to minimize the power load and prevent damage. Figure 3 shows the effect of illumination when a crystal with 0.2 mol % of Cr content has

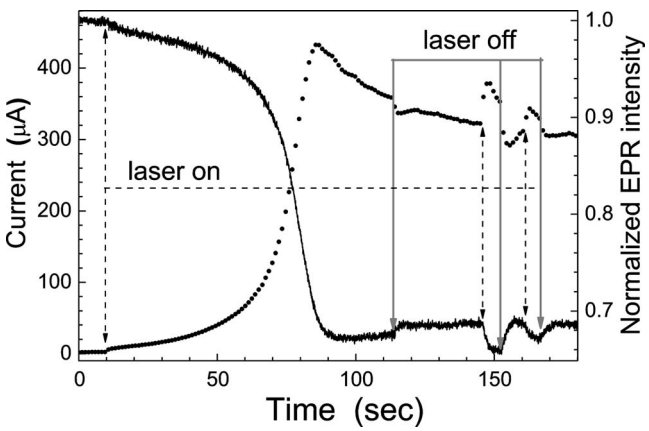

FIG. 3. Photocurrent (dots) and EPR intensity of Cr^{3+} (continuous line) in Cr-doped $SrTiO_3$ ([Cr]=0.1 mol %) as a function of time for a bias voltage of 200 V and laser irradiation (λ=633 nm).

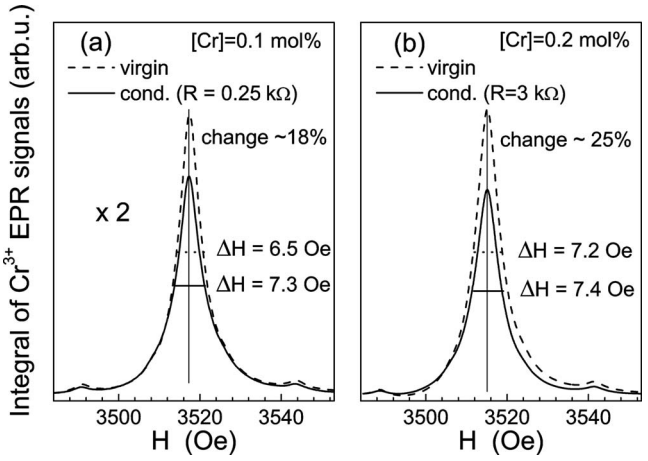

FIG. 4. Integral of the EPR Cr^{3+} signal in Cr-doped $SrTiO_3$ vs. magnetic field H. Comparison between the virgin (dashed line) and conducting crystals (continuous line).

reached a higher (intermediate) conducting state (1 M Ω) after ~ 2 h. At 200 V under laser illumination, the current increases and, simultaneously, the EPR intensity of Cr^{3+} decreases. Here we observe a decrease by $\sim 30\%$ of the initial EPR signal, whereas in the virgin state (see Fig. 1) the observed decrease is typically between 3% and 5%. Hence the transfer of electrons from the Cr ions to the CB can now be more effectively stimulated through impact ionization by the electrical current itself. The overshoot of the electrical current at ~ 90 s is not correlated with the EPR changes, indicating that at this stage, also other phenomena and/or other sources of carriers are involved. The photoexcited electrons involving the Cr centers are getting less dominant as revealed in subsequent on-off illumination cycles. The drastic resistance decrease by three orders of magnitude (gigaohm $\rightarrow$megaohm) can only be due to a substantial transformation of the bulk properties. Once the final conducting state is reached, the intensity of the Cr^{3+} signal has irreversibly dropped to a lower level. Figure 4 shows the integral of the Cr^{3+} EPR spectra of samples in the insulating and the conducting state for doping levels of 0.1 and 0.2 mol %, in which the EC process leads to final resistances of 0.25 and 3 kΩ, respectively. It can be seen that the total amount of Cr^{3+} is lowered by $\sim 20\%$. This change can be regarded as a measure of the volume fraction of the crystal that is irreversibly modified. The comparison between the virgin and conducting samples shows an increase of the full width at half maximum (FWHM) of $\Delta H \sim 1$ Oe in the sample with 0.1 mol % of Cr. For the sample with higher doping level (Fig. 4(b)), the FWHM remains apparently unchanged, because the linewidth is already broadened owing to the higher Cr content. The lineshape, however, is clearly asymmetric after the EC, indicating a small distortion of the Cr environment. In addition, there is evidence of electronic structural changes, as indicated by the reaction of the crystals to the laser illumination (without bias voltage) in the conducting state. Figure 5 shows that in this case the Cr^{3+} signal increases under laser exposure, whereas in the virgin state it decreased ([Cr]=0.1 mol %, same crystal as in Fig. 1). Process III (Fig. 2) explains this increase as a conversion of Cr^{4+} to Cr^{3+}. Therefore, the $\sim 20\%$ reduction in the Cr^{3+} signal in the conducting state is a proof of the creation of Cr^{4+} centers during the EC process. Apparently, the presence of mixed

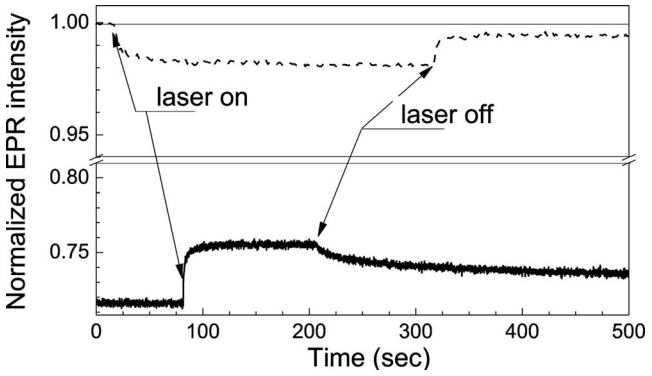

FIG. 5. Time-resolved EPR intensity of Cr^{3+} in Cr-doped $SrTiO_3$ ([Cr] =0.1 mol %) under laser exposure and without bias voltage for a sample in the virgin (dashed line) and the conducting (continuous line) state.

valencies of the Cr ions is necessary to create the conducting state. In oxidized samples, all Cr ions are in the 4+ valence state and no electron donors are present. Moreover, the Cr^{4+} ions act as electron traps, which explains why these samples cannot be brought into the conducting state through EC. An x-ray absorption spectroscopy (XAS) study of the Cr *K* edge (with a probing depth of $\sim 5\ \mu$m) shows[9] that for planar structures the EC process creates a Cr^{3+}/Cr^{4+} mixture.[3] From high-resolution imaging at the energy of the pre-edge of Cr, it is concluded that the conducting path exhibits an enrichment of V_O's located in the nearest-neighbor site of the Cr centers.[9] Such a defect should result in a paramagnetic center in a strong axial crystal field, which has been characterized for Fe^{3+}-V_O in $SrTiO_3$ and Cr^{3+}-V_O in WO_3.[10,11] In these cases, the strong axial field manifests itself in a large shift of the resonance field of the EPR signal by $\sim$2000 and $\sim$1000 Oe (when rotating the crystal axis from [100] to [010]) for $SrTiO_3$ and WO_3, respectively.[10,11] In our sample, however, this shift is absent, and only a small distortion was observed as deduced from the broadening by 1 Oe and the asymmetric EPR spectrum in Figs. 4(a) and 4(b), respectively. Such a small distortion of the oxygen octahedra surrounding the Cr is not compatible with the presence of V_O's at the nearest-neighbor position of Cr sites. Because EPR is a bulk-sensitive technique we cannot exclude the formation of a Cr^{3+}-V_O complex at the electrode interface as detected by XAS.

Through EPR studies we can directly observe the excitation of electrons from the Cr^{3+} ions to the CB via a decrease of the Cr^{3+} signal and a simultaneous increase of the electrical current at fixed bias. Therefore the Cr^{3+} ions present in the virgin insulating samples are responsible for the photocurrent observed that initiates the EC process. The drastic resistance decrease between the virgin and the final conducting state (gigaohm $\rightarrow$ kilo-ohm) can only be due to a substantial transformation of the bulk properties. Moreover, the decrease of the EPR signal by $\sim$20% in the conducting state indicates creation of Cr^{4+}, which could act as trap centers for the carriers. Apparently, the presence of mixed valences of the Cr ions is necessary to create the conducting state. This is in agreement with the result of luminescence measurements showing the recombination of electrons from the CB to the Cr^{4+} ions during the switching of conductivity to the high-resistance memory state.[2] The small distortions of the EPR spectra in the conducting state exclude the possibility of a Cr^{3+}-V_O complex in the bulk as a result of the EC that was proposed by others authors.[5,9]

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[1] Y. Watanabe, Ferroelectrics **349**, 190 (2007).
[2] S. F. Alvarado, F. L. Mattina, and J. G. Bednorz, Appl. Phys. A: Mater. Sci. Process. **89**, 85 (2007).
[3] G. I. Meijer, U. Staub, M. Janousch, S. L. Johnson, B. Delley, and T. Neisius, Phys. Rev. B **72**, 155102 (2005).
[4] A. Beck, J. G. Bednorz, C. Gerber, C. Rossel, and D. Widmer, Appl. Phys. Lett. **77**, 139 (2000).
[5] K. Szot, W. Speier, G. Bihlmeyer, and R. Waser, Nat. Mater. **5**, 312 (2006).
[6] W. S. Baer, Phys. Rev. **144**, 734 (1966).
[7] S. A. Basun, U. Bianchi, V. E. Bursian, A. A. Kaplyanskii, W. Kleemann, L. S. Sochava, and V. S. Vikhnin, Ferroelectrics **183**, 255 (1996).
[8] T. Feng, Phys. Rev. B **25**, 627 (1982).
[9] M. Janousch, G. I. Meijer, U. Staub, B. Delley, S. F. Karg, and B. P. Andreasson, Adv. Mater. (Weinheim, Ger.) **19**, 2232 (2007).
[10] E. S. Kirkpatrick, K. A. Müller, and R. S. Rubins, Phys. Rev. **135**, A86 (1964).
[11] T. Hirose and M. Kawaminami, J. Phys. Soc. Jpn. **50**, 843 (1981).